

Lead sulfate precursor to positive active material in lead/acid batteries

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Abstract

Lead/acid batteries occupy a very important position in the fields of secondary batteries for the higher performance and cost ratio. But when lead powder is used as a precursor to the active material, the production time is very long and the environmental pollution is very serious. Thus many people are seeking new material instead of lead powder. A new precursor to active material, lead sulfate, is studied in this paper. It follows the principles of cleaner production when lead sulfate is used as electrode material. The main advantages of lead sulfate as a precursor to positive active material is introduced. It shows from the battery performance test that it is completely practicable to use lead sulfate as a precursor to positive active material. The specific energy by weight of 12V10Ah battery at 5 and 2 h rate reaches 37.19 and 35.47 Wh kg⁻¹, respectively. The cycle life of 55% DOD attains 450 times. This has made it completely practicable as motive power sources for electric bicycles.

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1. Introduction

Although the specific energy by weight and volume of lead–acid batteries is inferior to that of Cd–Ni, Ni–MH, Li-ion and lithium polymer batteries, lead–acid batteries occupy a very important position in secondary batteries with high performance and cost ratio. The total output of chemical power sources in 1997 is US\$ 26.4 billion. The output of secondary batteries occupies 65% of the total output. The output of lead–acid batteries takes up 47% in all chemical power sources and 72% in secondary batteries [1]. Lead–acid batteries have the highest working voltage as well as better discharge performance with high current, high temperature and low temperature in aqueous power sources systems. What is more lead–acid batteries are suitable to both float use and cycle use. As a result they are extensively used in the fields of standby, energy reserve and motive power sources [2]. However in the production of traditional lead–acid batteries the pollution caused by lead and lead oxide powder has a very serious effect on the environments and workers. Consequently, people are trying their best to seek new, clean and safe material instead of lead powder [3]. The possibility of lead sulfate as a precursor to positive active material was studied in this article. In the meanwhile the valve-regulated

lead–acid batteries of 12V10Ah were prepared to testify the effect of lead sulfate on battery performances.

As a precursor to positive active material lead sulfate has the following advantages:

1. Higher paste porosity can be attained when lead sulfate is used as a precursor to positive active material. The densities and molar volumes of some lead compounds are listed in Table 1 [4].

It can be seen from Table 1 that lead sulfate has the smallest density of 6.32 g cm⁻³ and the biggest molar volume of 48.2 cm³ mol⁻¹ in all lead compounds. As a result the lead sulfate-based pastes exhibit greater molar-volume shrinkage during formation than do the oxide-based pastes and, thus, have greater porosity in the final active material that is lead dioxide. For example, converting lead sulfate to lead dioxide results in a 48% volume shrinkage versus about 9% shrinkage when converting lead oxide to lead dioxide. Increasing the porosity can cause more electrolytes to diffuse into the depth of the plates. On the other hand it can reduce the encapsulation of lead dioxide by lead sulfate during discharge, and thus help maintain surface area of the reaction sites as well as conductivity [5]. All this is beneficial to improve the utilization efficiency of active mass.

2. Lead powder in lead/acid batteries is not pure lead but the mixture of lead and lead oxide. Usually there is about

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Table 1
Densities and molar volumes of some lead compounds

Lead compounds	Density (g cm^{-3})	Molar volume ($\text{cm}^3 \text{mol}^{-1}$)
PbSO_4	6.32	48.2
$\text{PbO} \cdot \text{PbSO}_4$	7.02	38.0
$3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$	6.50	38.0
PbO_2	9.375	25.15
Pb	11.34	18.27

15–30% of free lead in lead powder. The oxidation degree difference inevitably exists for some reasons such as temperature. This will influence the amount of acid and water absorbed by lead powder. What is more, the free lead in lead powder will undergo more oxidation during the following paste mixing, curing and drying. Due to the difference of the amount of oxidative lead in every step it will result in the difference of plate qualities. All this will lead to the difference of assembled battery voltages and battery capacities. However, the above problem does not arise when lead sulfate is used as a precursor to positive active material. Thus the uniformity of the plate qualities and that of capacities as well as assembled voltages are ensured.

- The production process can be simplified and producing time can be saved when lead sulfate is used as a precursor to positive active material. Curing is a very important and necessary step in the production of traditional lead–acid batteries. The function of curing mainly lies in reducing the content of free lead to a level below 5% and nearer 1%. Failure to oxidize the free lead to below 5% may result in unacceptably formed plates [6]. Thus the pastes must be cured to avoid this problem. But the curing process is time consuming and costly. Typically, a curing cycle of up to 3 days is required to arrive at a free lead content below 5% and preferably not more than 1%. Further, this curing process must be done under rigidly controlled temperature and humidity conditions. However, when lead sulfate is adopted, curing step can be neglected because there is no free lead. Consequently, the time, electric energy, human resources and machine consumed by curing process can be saved.
- Sulfuric acid with a high concentration is needed during the course of paste mixing in the production of traditional lead–acid batteries. A large amount of heat gives out when sulfuric acid reacts with lead powder. As a result cooling measures must be taken. Corrosion of the machine is very serious and the pasting time is prolonged. But when lead sulfate is adopted, sulfuric acid with a low concentration is used. Therefore the above problem caused by lead powder will not occur.
- Electric energy can be saved when lead sulfate is used as starting positive active material. The theoretical electric quantity needed for transforming 1 kg components into PbO_2 is listed in Table 2 [7].

Table 2
The theoretical electric quantity needed for transforming 1 kg components into PbO_2

Components	Electric quantity (Ah)
PbO	240
PbSO_4	176
Pb	514

It can be seen from Table 2 that the electric quantity needed for transforming lead oxide or pure lead into lead dioxide is much more than lead sulfate.

2. Experiments

2.1. Preparation of lead sulfate

Lead sulfate can industrially be obtained through the reaction of sulfuric acid with lead ores [8]. For convenience lead sulfate is made through the reaction of sulfuric acid with lead powder in this experiment. The reaction can be carried out in the sealed reactor. Excessive sulfuric acid with the density of 1.28 g cm^{-3} is added to the lead powder. The reactants are continuously mixed until they become completely white. The reaction needs about 2 days and the temperature is controlled at $50\text{--}70^\circ\text{C}$. The reacting products are washed in distilled water until the pH value reaches 7. The filtered products is dried 24 h in the drier of 50°C .

2.2. Preparation of plates

The negative grid alloys are composed of ordinary lead–calcium–tin–aluminum. The prescription of the negative plates is supplied by Hangzhou Narada Power Sources Group. The size of the negative plates is $69 \text{ mm} \times 45 \text{ mm} \times 2.0 \text{ mm}$. The positive grid alloys are made up of low calcium and high tin alloys. The aim is to improve the conductivity of grids and charging acceptance after deep discharge. The size is $69 \text{ mm} \times 45 \text{ mm} \times 2.2 \text{ mm}$. The prescription of lead sulfate paste is listed in Table 3.

The density of sulfuric acid is 1.05 g cm^{-3} . A is a kind of inorganic conductive additive, which can improve the conductivity of active mass. B is a kind of organic additive, which can strengthen the adhesion between grids and active mass. At the same time according to the traditional techniques ordinary plates are prepared. Hangzhou Narada Power Sources Group provides the ordinary positive plate

Table 3
The prescription of lead sulfate paste

	Material					
	PbSO_4	H_2SO_4	H_2O	Fiber	A	B
Amount (kg)	70	12	8	0.06	3.5	2

prescription that is the mixture of lead powder, sulfuric acid, water and fiber.

The lead sulfate-based positive plates are dried for 2 h in the oven of 60 °C. The ordinary positive plates undergo curing and drying. The formation is container formation. Ten positive plates and 11 negative plates are placed in one container. The density of sulfuric acid is 1.05 g cm⁻³. The algorithm is charging 24 h at 1.5 A, then charging 20 h at 0.8 A and finally charging 20 h at 0.4 A.

2.3. Preparation of 12V10Ah VRLA batteries

The size of the battery case is 151 mm × 98 mm × 100 mm. Each cell contains eight positive plates and nine negative plates. Only positive plates are wrapped with AGM separators. The size of separators is 150 mm × 50 mm × 1.0 mm and the assembling pressure is 50 kPa. The amount of electrolyte in each cell is 100 ml sulfuric acid with the density of 1.3 g cm⁻³ and 1.5 g sodium sulfate. The charging algorithm is constant voltage and limited current. The voltage is 14.7 V and the current is 1.8 A.

2.4. Test of the paste apparent density

Put the mixed paste into the specially made vessel with the volume of 100 cm³. Vibrate the vessel slightly and make the level of paste and that of the vessel flush. Measure the weight of the vessel, W_1 , and that of the paste adding to the vessel, W_2 , respectively. The paste apparent density can be obtained through the following equation:

$$\text{Apparent density (g cm}^{-3}\text{)} = \frac{W_2 - W_1}{100}$$

2.5. Test of the porosity of positive plates

The porosity test is carried out by methods of benzene displacing density. During the experiment put the dried positive plates with the lugs cut in the vacuum for 30 min at first. Then take the plates out and dip into the beaker filled with benzene. Measure the weight of beaker, W_1 , that of the beaker full of benzene, W_2 , that of the positive plates, W_3 , and that of the beaker full of benzene and positive plates, W_4 . We can get the benzene weight occupied by positive plates, W , from the following equation:

$$W = W_1 + W_2 + W_3 - W_4$$

The volume of active material and grid, V_1 , can be obtained through the equation

$$V_1 = \frac{W}{\rho}$$

where ρ is the benzene density.

Thus we can get the porosity of plates, P :

$$P = 1 - \frac{V_1}{V_2}$$

where V_2 is the apparent volume of the positive plates.

2.6. The initial 5 and 2 h rated capacity test of batteries

The full charged batteries are put in the 25 °C water bath for 1–2 h. Then the batteries are discharged at 5 h rated current of 2.08 A and 2 h rated current of 5 A until the end of discharging voltage is 10.5 V, respectively. The charging and discharging equipment is Bitrode LCN.

2.7. The cycle life test of batteries at 55% DOD

In the 25 °C water bath the full charged battery is discharged at 2.75 I_5 , i.e. 5.72 A for 1 h and then charged at the voltage of 14.7 V and the current of 0.75 I_5 , i.e. 1.56 A for 5 h. This forms a whole cycle. The 5 h rated capacity is tested every 25th cycle. The test is completed when the battery capacity is less than 70% of the 5 h rated nominal capacity.

3. Results and discussion

3.1. The apparent density of the paste

The apparent density of lead sulfate paste is 3.15 g cm⁻³ while that of ordinary paste is 4.20 g cm⁻³. The lower density of new paste reduces the paste amount when the grid volume is constant. In the meanwhile the porosity is increased.

3.2. The porosity of positive plates

The porosity of positive plates using lead powder is 52.3% while that using lead sulfate is 58.5%. As a result of the higher porosity of positive plates using lead sulfate, sulfuric acid can diffuse to the depth of the plates and the utilization is improved.

3.3. The content of lead dioxide in positive plates after formation

The positive plates using lead sulfate contain 92.3% of lead dioxide after formation. It shows that it is completely practicable to use lead sulfate as positive active material and the transformation efficiency is very high.

3.4. XRD analysis of plates after formation

The XRD spectroscopy of plates after formation is shown in Fig. 1. The main material in the plates after formation is β -PbO₂. The utilization of active mass is higher due to the higher β -PbO₂ content in the plates.

3.5. The results of the capacity test

The discharging curves of the batteries with the ordinary paste and lead sulfate paste at 5 h rate and 2 h rate are shown in Figs. 2 and 3, respectively.

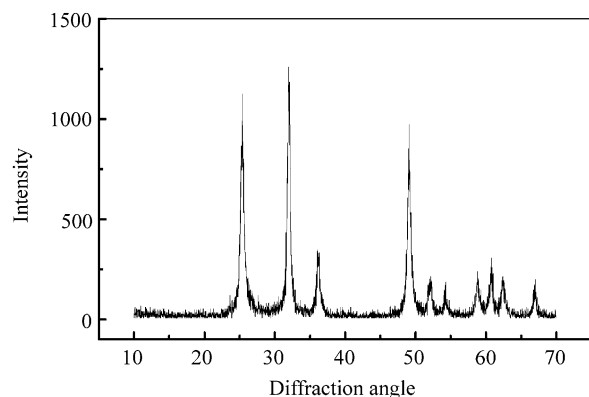


Fig. 1. XRD spectroscopy of plates after formation.

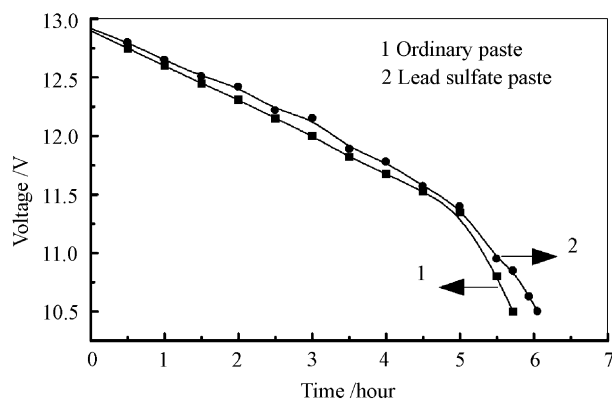


Fig. 2. Discharging curve at 5 h rate.

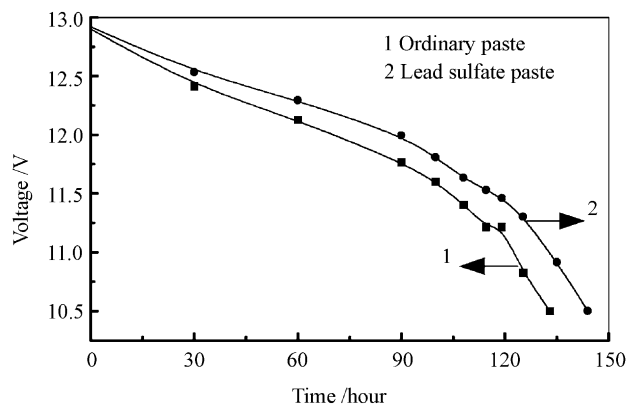


Fig. 3. Discharging curve at 2 h rate.

It can be seen from Fig. 2 that the discharging time with ordinary paste is 5 h 43 min at 5 h rate while the discharging time with lead sulfate paste is 6 h and 3 min. The relevant specific energy by weight at 5 h rate is 33.2 and 37.19 Wh kg⁻¹, respectively.

It can also be seen from Fig. 3 that the discharging time with ordinary paste is 2 h and 13 min at 2 h rate while the discharging time with lead sulfate paste is 2 h and 24 min. The relevant specific energy by weight at 2 h rate is 30.93 and 35.47 Wh kg⁻¹, respectively.

3.6. The results of cycle life

The battery with ordinary paste has a cycle life of 402 times at 55% DOD while the battery with lead sulfate paste reaches 450 times.

4. Conclusions

It shows from the performance test of the battery that it is thoroughly practicable to use lead sulfate as starting positive active material. The porosity of plates attains 58.5%. The specific energy by weight of 5 and 2 h rate is 37.19 and 35.47 Wh kg⁻¹, respectively. The cycle life at 55% DOD is 450 times. This has completely met with the requirements of electric bicycles for lead–acid motive power sources. Lead sulfate as starting negative active material and the methods of improving cycle life of the lead sulfate-based battery are still under research.

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